K. K. Dagde, Y. T. Puyate / International Journal of Engineering Research and Applications (IJERA) ISSN: 2248-9622 www.ijera.com
Vol. 2, Issue 6, November- December 2012, pp.557-568

Six-lump kinetic modelling of adiabatic plug-flow riser-reactor in an industrial FCC unit

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Abstract

A six-lump kinetic model is presented that describes the catalytic cracking reactions taking place in an industrial riser-reactor. In this scheme, C3's (propane and propylene gases) and C4's (butane and butylenes gases) components of liquefied petroleum gas are predicted independently, as well as gasoline, dry gas, and coke. The riser-reactor is modelled as a plug-flow reactor operating adiabatically. Model-predicted yields of gasoline, C3's, C4's, fuel gas, coke, and riser-reactor outlet-temperature, agree reasonably well with plant data obtained from an operating industrial riser-reactor. Sensitivity analysis carried out on the riser-reactor indicates that inlet-temperature of gas-oil (feed), catalyst-to-gas oil ratio, and mass flowrate of gas-oil, are important process variables that affect the operation of the riser-reactor. It is shown that the minimum catalyst-to-gas oil ratio required for maximum conversion of gas-oil is 3. Simulation results using catalyst-to-gas oil ratio of 6.5, inlet-temperature of gas-oil of 505K, and mass flowrate of gas-oil of 67.8 kg/s, give yields of 45.81% gasoline, 6.32% C3's, 10.68% C4's, 5.42% fuel gas, 5.11% coke, and 26.66% of unconverted gas-oil.

Keywords: Riser-reactor; modelling; catalytic cracking; lump; kinetics

1. Introduction

Crude oil contains hydrocarbons ranging from light gases and liquefied petroleum gas (LPG) to residues boiling above 616K [1]. These products of various boiling points can be separated using a distillation column. However, distillation alone cannot produce sufficient amount of lighter fractions such as gasoline to meet public demand. Thus, subsequent refining process known as fluid catalytic cracking (FCC) is used and forms the heart of a modern refinery oriented towards maximum gasoline production. Fluid catalytic cracking, which takes place in the presence of a catalyst, is a process whereby heavier distillates of crude oil such as vacuum gas-oil (VGO) and other related heavy stocks are converted into lighter products such as high octane gasoline, light cycle oil, and gaseous products (LPG, fuel gas, etc.), as well as coke. The FCC process comprises mainly two reactors: (1) a riser-reactor, where high molecular weight hydrocarbons come in contact with a catalyst and are cracked into lower molecular weight products with simultaneous deposition of coke on the catalyst, and (2) a regenerator-reactor, where the coke deposits on the catalyst are burnt-off using air and the regenerated catalyst is returned to the riser-reactor to partly supply the heat required for the endothermic cracking reactions.

The riser-reactor is probably the most important equipment in a FCC plant because all cracking reactions and fuel formation occur in this reactor. A mathematical model describing the operations in a riser-reactor can be a valuable tool for optimizing the performance of the riser-reactor in order to obtain higher yield of products. The first problem in the modelling of FCC riser-reactor is selection of the kinetics scheme. One approach that deals with multi-component mixtures like gas-oil which contains more than 10,000 different species is the formulation of lumped kinetic schemes [2, 3, 4]. In a three-lump kinetic model, gas-oil (i.e. the feed, and taken as one lump) is converted into light gases plus coke lump, and gasoline [5]. Subsequent studies in the literature [6, 7, 8, 9] considered the need to present coke and light gases as separate lumps creating a four-lump kinetic model in which gas-oil is converted into light gases (C1-C4), coke, and gasoline; and a five-lump kinetic model in which gas-oil is converted into coke, gasoline, LPG (C3-C4), and fuel gases (dry gases, i.e. C1-C2). A major issue that is common with the analyses presented in the literature for each of these kinetic models is that only the kinetic parameters are determined but not applied to simulate a functional riser-reactor in an industrial FCC unit.

Oboho et al. [10] simulated an industrial fluidized-bed FCC riser-reactor using a three-lump kinetic model, but the coke generated during the cracking reactions could not be determined independently in the analysis. Since the heat required for the cracking reactions is obtained partly by burning-off the coke deposited on the catalyst in the regenerator, adequate prediction of the amount of coke on the catalyst is imperative during kinetic modelling of a riser-reactor. In order to account for coke formation on the catalyst, Oboho et al. [11] and Oboho and Akpa [12] presented a four-lump kinetic model to account for the coke formation on the catalyst. But the weakness of the four-lump model is that the LPG and fuel gases are lumped together as light gases, which makes it impossible to consider individual effects of LPG and fuel gases on the kinetic scheme. This disadvantage of the four-lump model was taken care of in a five-lump kinetic model presented by Dagde et al. [13], where gas-oil is converted into gasoline, LPG, dry gas, and coke. However, the five-lump scheme could not determine separately the C_3's (propane and propylene gases) as well as C_4's (butane and butylene gases) which are lumped in the LPG.

In this work, a six-lump kinetic scheme for an adiabatic plug-flow riser-reactor is presented in which gas-oil is converted into dry gas, coke, gasoline, C_3's, and C_4's. Such a kinetic scheme allows independent prediction of C_3's and C_4's which have valuable domestic and laboratory applications, used as feedstock in the petrochemical industry, and in compressor and air blower design [3].

2. The six-lump kinetic model

The six-limp kinetic model shown in Fig. 1 and proposed by Ancheyta and Sotelo [14] is used in this study. The model assumes that gas-oil (1) is converted to (2) gasoline (C5+), (3) C4's (butane, I-butane and butene), (4) C3's (propane and propylene), (5) dry gas (C1 – C2), and (6) coke, as well as unconverted VGO (decanted and light cycle oils). The kinetics of VGO cracking has been found experimentally to follow closely a second-order chemical reaction [5], while the cracking of gasoline and LPG (C3's and C4's) follow a first-order chemical reaction [2, 3, 4].

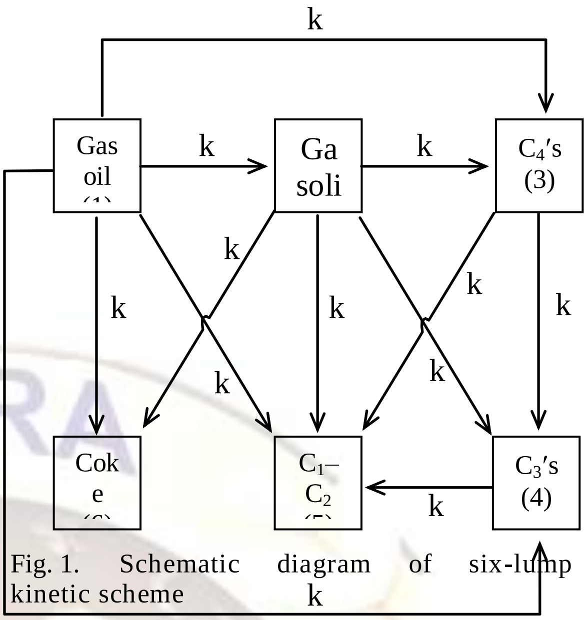

Fig. 1. Schematic diagram of six-lump kinetic scheme

The following rate equations are formulated for the various components of the six-lump kinetic model shown in Fig. 1:

$$(-r_1) = (k_{12} + k_{13} + k_{14} + k_{15} + k_{16})\, y_1^2\, \phi\, \eta_{ss} \qquad (1)$$

$$(-r_2) = [(k_{23} + k_{24} + k_{25} + k_{26})\, y_2 - k_{12}\, y_1^2]\phi\eta_{ss} \qquad (2)$$

$$(-r_3) = [(k_{34} + k_{35})\, y_3 - k_{23}\, y_2 - k_{13}\, y_1^2]\phi\eta_{ss} \qquad (3)$$

$$(-r_4) = [k_{45}\, y_4 - k_{24}\, y_2 - k_{34} y_3 - k_{14}\, y_1^2]\phi\eta_{ss} \qquad (4)$$

$$(-r_5) = [-k_{15}\, y_1^2 - k_{25}\, y_2 - k_{35}\, y_3 - k_{45}\, y_4]\phi\eta_{ss} \qquad (5)$$

$$(-r_6) = (-k_{16} y_1^2 - k_{26} y_2)\,\phi\,\eta_{ss} \qquad (6)$$

where k_{ij} are the rate constants for the cracking of lumps i to j; $(-r_i)$ are the reaction rates with respect to lumps i, with $i = 1,$ 2, 3, 4, 5, 6; $y_i = \rho_i / \rho_T$ are the mass fractions of the various lumps, with ρ_i as the mass densities of the different lumps, and ρ_T is the total mass density of all the six lumps; η_{ss} is the effectiveness factor; and ϕ is the catalyst deactivation function. The deactivation kinetic model of Weekman and Nace [5] is chosen in this study because of its simplicity and popularity in FCC modelling, where the decay of catalyst activity due to coke deposition is represented by the catalyst deactivation function expressed in the form

$$\phi = \exp(-k_d\ t_c) \qquad (7)$$

where k_d is the catalyst decay coefficient which is related to the riser-temperature in the Arrhenius equation

$$k_d = k_{do} \exp(-E / RT) \qquad (8)$$

and t_c is the catalyst residence time expressed as [15]

$$t_c = \frac{A_R L_R \rho_{cat}}{F_o \times (CTO)} \qquad (9)$$

where k_{do} is the catalyst decay pre-exponential kinetic factor, F_o is the mass flowrate of gas-oil, (CTO) is the catalyst-to-gas oil ratio, $\rho_{cat.}$ is the mass density of catalyst, A_R is the cross-sectional area of the riser-reactor, L_R is the height of the riser-reactor, R is the universal gas constant, and T is the absolute temperature. Substituting eq. (9) into eq. (7) gives

$$\phi = \exp\left[\frac{-k_d\ \rho_{cat}\ A_R\ L_R}{F_o \times (CTO)}\right] \qquad (10)$$

The effectiveness factor (η_{ss}) for the catalytic cracking of vacuum gas-oil is evaluated as [16]:

$$\eta_{ss} = \frac{\tanh(h_i)}{h_i} \qquad (11)$$

where h_i is a modified Thiele modulus given as

$$h_i = \frac{1}{a_{ext}}\sqrt{\frac{(n+1)}{2}\ \frac{\rho_{cat}\,\phi k_i\, C_i^{n-1}}{D_{eff}}} \qquad (12)$$

where n is the order of reaction (equal to 2 for gas-oil cracking); α_{ext} is the catalyst-specific external surface area; k_i are the kinetic rate constants of the respective lumps; D_{eff} is the effective diffusivity of gas-oil through the catalyst, and C_i is the molar concentration of the various lumps.

It is important to note that α_{ext} in eq. (12) can be defined using the characteristic dimension, L_Z, of the Zeolite crystallite (i.e. catalyst particle size) since all the cracking reactions take place in the Zeolite crystallite with little influence from the matrix of the catalyst [17]. Therefore, approximating the crystallite geometry to be a sphere, gives the catalyst-specific external surface area as [4]

$$\alpha_{ext} = \frac{6}{L_Z} \qquad (14)$$

which when substituted into eq. (12) yields the following expression for gas-oil:

$$h_o = \frac{L_Z}{6}\sqrt{\frac{3}{2}\ \frac{\rho_{cat}\ \phi\ (k_{12}+k_{13}+k_{14}+k_{15}+k_{16})\ C_o}{D_{eff}}} \qquad (15)$$

where the subscript “o” indicates gas-oil. It is expected that diffusion of gas-oil takes place in a USY Zeolite, and the effective diffusion coefficient of gas-oil (D_{eff}) is given by the Erying equation [18].

$$D_{eff} = D_p \exp\left(-E_D / RT\right) \qquad (16)$$

where D_p is the pre-exponential factor for diffusion, and E_D is the activation energy for diffusion. A value of $D_p = 9.58 * 10^{13}\left(m^2/s\right)$ and $E_D = 237.66\left(kj/mol\right)$ were used [4].

2.1. The riser-reactor model

In the derivation of the mathematical model for the riser-reactor, the following assumptions are made:

Axial dispersion in the riser-reactor is neglected.
Catalyst particles have a uniform size in a given differential element, and both gas-oil and gasoline have identical catalyst deactivation function, ϕ [2].
The riser wall is adiabatic
Feed viscosity and specific heat capacities of all components are constant.
Adsorption and dispersion inside the catalysts particles are negligible.
Pressure changes throughout the riser height are due to static head of catalyst in the riser.
Coke deposition on the catalyst does not affect the fluid flow.
In each section of the riser-reactor, the catalyst and gas have the same temperature.
The coke has the same specific heat as the catalyst.
The riser dynamics is fast enough to justify plug-flow characteristics and a quasi-steady state model.
Instantaneous vaporization occurs at the entrance of the riser-reactor [19].
Cracking reactions are completed in the riser-reactor,ce hence no reaction takes place in the stripping section.

Applying the conservation principle to a control volume ($A_R dL$) of a plug-flow riser-reactor based on the above assumptions, where dL is the differential height of the reactor’s control volume, gives the mass and energy balances as

$$-\frac{dy_1}{dt}=-U\frac{dy_1}{dL}=(-r_1)\varepsilon_R$$
$$=(k_{12}+k_{13}+k_{14}+k_{15}+k_{16})\,y_1^2\,\phi\,\varepsilon_R\eta_{ss} \quad (17)$$

$$-\frac{dy_2}{dt}=-U\frac{dy_2}{dL}=(-r_2)\varepsilon_R$$
$$=[(k_{23}+k_{24}+k_{25}+k_{26})\,y_2-k_{12}\,y_1^2]\phi\,\varepsilon_R\,\eta_{ss} \quad (18)$$

$$-\frac{dy_3}{dt}=-U\frac{dy_3}{dL}=(-r_3)\varepsilon_R$$
$$=[(k_{34}+k_{35})\,y_3-k_{23}y_2-k_{13}\,y_1^2]\phi\,\varepsilon_R\,\eta_{ss} \quad (19)$$

$$-\frac{dy_4}{dt}=-U\frac{dy_4}{dL}=(-r_4)\varepsilon_R$$
$$=[k_{45}\,y_4-k_{24}\,y_2-k_{24}y_2-k_{14}\;y_1^2]\phi\;\varepsilon_R\,\eta_{ss} \quad (20)$$

$$-\frac{dy_5}{dt}=-U\frac{dy_5}{dL}=(-r_5)\varepsilon_R$$
$$=[-k_{15}\,y_1^2-k_{25}\,y_2-k_{35}\,y_3-k_{45}\,y_4]\phi\;\varepsilon_R\,\eta_{ss} \quad (21)$$

$$-\frac{dy_6}{dt}=-U\frac{dy_6}{dL}=(-r_6)\varepsilon_R$$
$$=(k_{16}y_1^2+k_{26}y_2)\phi\,\varepsilon_R\,\eta_{ss} \quad (22)$$

$$-\frac{dT_R}{dL}=\frac{\phi\,\varepsilon_R\,\rho_o\,A_R}{(F_{cat}\,C_{pcat}+F_o\;C_{po})}\times$$
$$\begin{bmatrix} y_1^2\begin{bmatrix}k_{12}(\Delta H_{12})+k_{13}(\Delta H_{13})+k_{14}(\Delta H_{14})+\\ k_{15}(\Delta H_{15})+k_{16}(\Delta H_{16})\end{bmatrix} \\ +\,y_2\begin{bmatrix}k_{23}(\Delta H_{23})+k_{24}(\Delta H_{24})+k_{25}(\Delta H_{25})\\ +k_{26}(\Delta H_{26})\end{bmatrix}+ \\ y_3\left[k_{34}(\Delta H_{34})+k_{35}(\Delta H_{35})\right]+\;y_4\left[k_{45}(\Delta H_{45})\right] \\ \end{bmatrix} \quad (23)$$

where y_i is the mass fraction of lump i, ε_R is the average void fraction in the riser-reactor, U is the riser superficial velocity, F_{cat} is the mass flowrate of catalyst, C_{pcat} and C_{po} are the specific heat capacities of catalyst and gas-oil respectively, and ΔH_{ij} are the heat of reaction for cracking lumps i to j, and t is time.

Since gas-oil is the feed that is cracked into the various products, the mass fraction of gas-oil at the inlet ($L=0$) of the riser-reactor is unity, while the mass fractions of the products at the inlet are equal to zero because no product is formed at the inlet of the riser-reactor. Also, at the inlet of the riser-reactor, the feed temperature is taken to be a reference temperature (T_{ref}) equal to 800K [20]. These boundary conditions at the inlet of the riser-reactor are defined mathematically as

$$L=0:\quad \begin{cases} y_1=1 \\ y_i=0 \qquad i=2,\,3,\,4,\,5,\,6 \\ T_R=T_{ref}\end{cases} \quad (24)$$

We define the following dimensionless variables

$$Z=\frac{L}{L_R} \quad (25)$$

$$\theta_R=\frac{T_R}{T_{ref}} \quad (26)$$

where Z is the dimensionless height of the riser-reactor, L is the variable height of the riser-reactor, θ_R is the dimensionless riser temperature, and T_R is the riser temperature. Using eqs. (25) and (26) in eqs. (17) – (23), and noting that

$$U=\frac{\vartheta_o}{A_R}=\frac{F_o}{\rho_o A_R} \quad (27)$$

gives

$$\frac{dy_1}{dZ}+\frac{\phi\,A_R\,\varepsilon_R\,L_R\,\rho_o}{F_o}$$
$$(k_{12}+k_{13}+k_{14}+k_{15}+k_{16})\,y_1^2\,\eta_{ss}=0 \quad (28)$$

$$\frac{dy_2}{dZ}+\frac{\phi\,A_R\,\varepsilon_R\,L_R\,\rho_o}{F_o}$$
$$[(k_{23}+k_{24}+k_{25}+k_{26})y_2-k_{12}\,y_1^2]\,\eta_{ss}=0 \quad (29)$$

$$\frac{dy_3}{dZ}+\frac{\phi\,A_R\,\varepsilon_R\,L_R\,\rho_o}{F_o}$$
$$[(k_{34}+k_{35})y_3-k_{23}\,y_2-k_{13}\,y_1^2]\,\eta_{ss}=0 \quad (30)$$

$$\frac{dy_4}{dZ}+\frac{\phi\,A_R\,\varepsilon_R\,L_R\,\rho_o}{F_o}$$
$$[k_{45}\,y_4-k_{24}\,y_2-k_{34}y_3-k_{14}\;\;y_1^2]\,\eta_{ss}=0 \quad (31)$$

$$\frac{dy_5}{dZ}+\frac{\phi\,A_R\,\varepsilon_R\,L_R\,\rho_o}{F_o}$$
$$[-k_{15}\,y_1^2-k_{25}\,y_2-k_{35}\,y_3-k_{45}\,y_4]\eta_{ss}=0 \quad (32)$$

$$\frac{dy_6}{dZ}+\frac{\phi\,A_R\,\varepsilon_R\,L_R\,\rho_o}{F_o}\quad(k_{16}y_1^2-k_{26}y_2)\,\eta_{ss}=0 \quad (33)$$

$$\frac{d\theta_R}{dZ}+\frac{\phi\,\varepsilon_R\,L_R\rho_o\,A_R}{(F_{cat}\,C_{pcat}+F_o\;C_{po})T_{ref}}\times$$
$$\begin{bmatrix} y_1^2\begin{bmatrix}k_{12}(\Delta H_{12})+ \qquad\qquad +k_{15}(\Delta H_{15})\\ k_{13}(\Delta H_{13})+k_{14}(\Delta H_{14})+k_{16}(\Delta H_{16}\end{bmatrix} \\ +\,y_2\begin{bmatrix}k_{23}(\Delta H_{23})++k_{25}(\Delta H_{25})\\ k_{24}(\Delta H_{24})\quad+k_{26}(\Delta H_{26})\end{bmatrix} \\ +\;y_3\left[k_{34}(\Delta H_{34})+k_{35}(\Delta H_{35})\right] \\ +\;y_4\left[k_{45}(\Delta H_{45})\right]\end{bmatrix}=0 \quad (34)$$

and the boundary conditions (24) become

$$Z = 0: \begin{cases} y_1 = 1 \\ y_2 = y_3 = y_4 = y_5 = y_6 = 0 \\ \theta_R = 1 \end{cases} \qquad (35)$$

where ϑ_0 is the volumetric flow rate of gas-oil. Equation (28)–(34) were solved numerically using a fourth-order Runge-Kutta algorithm using the boundary conditions (35).

3. Estimation of kinetic parameters

The riser-reactor model equations contain unknown kinetic parameters such as the reaction rate constants (k_{ij}) for the various reaction paths, and the catalyst deactivation function (ϕ). These constants have to be determined before equations (28)-(34) can be integrated. The kinetic parameters for the cracking reactions based on the six-lump kinetic model are presented in Table 1.

Table 1. Estimated kinetic parameters for cracking reactions in the riser-reactor [15]

Reaction path	**Pre-exponential constant (s^{-1})**	**Activation energy (kJ/kmol)**	**Heat of reaction (kJ/kg)**	**Stoichiometric coefficient (V_{ij})**
Gas-oil to gasoline (k_{12})	562	46240	8010	3.28
Gas-oil to C_4 LPG (k_{13})	77	59750	2000	13.13
Gas-oil to C_3 LPG (k_{14})	23	59750	876000	22.31
Gas-oil to dry gas (k_{15})	465	59750	790000	20.98
Gas oil to coke (k_{16})	96	78490	200	0.97
Gasoline to C_4 LPG (k_{23})	164	78490	20000	4.00
Gasoline to C_3 LPG (k_{24})	157	59750	100	6.81
Gasoline to Dry gas (k_{25})	11	46240	10760	6.4
Gasoline to coke (k_{26})	165	16150	2800	6.3
C_4 LPG to C_3 LPG (k_{34})	65	50750	5400	0.30
C_4 LPG to Dry gas (k_{35})	10	78490	1700	1.7
C_3 LPG to Dry gas (k_{45})	12	59750	100	1.6
Catalyst decay (k_d) (Lee et al., 1989)	83806	117705		0.94

The reaction rate constants are functions of temperature generally given by the Arrhenius relation (Levenspiel, 1999)

$$k_{ij}' = k_{io} \exp\left(\frac{-E_i}{RT}\right) \qquad (36)$$

where the prime indicates values of k_{ij} predicted by eq. (36), K_{io} are the pre-exponential kinetic constants for the respective lumps, and E_i are the activation energies of the different lumps. The rate constants (k_{ij}), and the stoichiometric coefficients (V_{ij}) of the various lumps are expressed as (Dagde, 2009)

$$k_{12} = V_{og} k_{12}', \quad V_{og} = \frac{M_o}{M_g} \qquad (37)$$

$$k_{13} = V_{oC_4} k_{13}', \quad V_{oC_4} = \frac{M_o}{M_{C_4}} \qquad (38)$$

$$k_{14} = V_{oC_3} k_{14}' \quad V_{oC_3} = \frac{M_o}{M_{C_3}} \qquad (39)$$

$$k_{15} = V_{od} k_{15}', \quad V_{od} = \frac{M_o}{M_d} \qquad (40)$$

$$k_{16} = V_{oc} k_{16}', \quad V_{oc} = \frac{M_o}{M_c} \qquad (41)$$

$$k_{23} = V_{gC_4} k_{23}', \; V_{gC_4} = \frac{M_g}{M_{C_4}} \qquad (42)$$

$$k_{24} = V_{gC_3} k_{24}', \; V_{gC_3} = \frac{M_g}{M_{C_3}} \qquad (43)$$

$$k_{25} = V_{gd} k_{25}', \quad V_{gd} = \frac{M_g}{M_d} \qquad (44)$$

$$k_{26} = V_{gc} k_{26}', \quad V_{gc} = \frac{M_g}{M_c} \qquad (45)$$

$$k_{34} = V_{C_4C_3} k_{34}', \; V_{C_4C_3} = \frac{M_{C_4}}{M_{C_3}} \qquad (46)$$

$$k_{35} = V_{C_4d} k_{35}', \; V_{C_4d} = \frac{M_{C_4}}{M_d} \qquad (47)$$

$$k_{45} = V_{C_3d} k'_{45}, \; V_{C_3d} = \frac{M_{C_3}}{M_d} \qquad (48)$$

where M_o is the molecular weight of gas-oil, M_g is the molecular weight of gasoline, M_{C_4} is the molecular weight of LPG (C_4), M_{C_3} is the molecular weight of LPG (C_3), M_c is the molecular weight of coke, M_d is the molecular weight of dry gas, V_{og} is the stoichiometric ratio of gas-oil to gasoline, V_{oC_4} is the stoichiometric ratio of gas-oil to C_4, V_{oC_3} is the stoichiometric ratio of gas-oil to C_3, V_{od} is the stoichiometric ratio of gas-oil to dry gas, V_{oc} is the stoichiometric ratio of gas-oil to coke, V_{gC_4} is the stoichiometric ratio of gasoline to C_4, V_{gC_3} is the stoichiometric ratio of gasoline to C_3, V_{gd} is the stoichiometric ratio of gasoline to dry gas, V_{gc} is the stoichiometric ratio of gasoline to coke, $V_{C_4C_3}$ is the stoichiometric ratio of C_4 to C_3, V_{C_4d} is the stoichiometric ratio of C_4 to dry gas, and V_{C_3d} is the stoichiometric ratio of C_3 to dry gas. Table 2 shows the average molecular weights of the six lumps used in the study.

Table 2. Average molecular weights of the six lumps [21, 22]

Lump	**Average molecular weight (kg/kmol)**
Gas–oil	$M_o = 386\,*$
Gasoline	$M_g = 117.8\,**$
LPG (C_4)	$M_{C_4} = 29.4\,**$
LPG (C_3)	$M_{C_3} = 17.3\,**$
Dry gas	$M_d = 18.4\,**$
Coke	$M_c = 400\,**$

4. Properties of feed and products, and dimensions of some components of FCC unit

The properties of feed and products of the six-lump catalytic cracking process, and the dimensions of some components of FCC unit, are presented in Tables 3 and 4 respectively. The feedstock composition is given in Table 5, while the physical properties of the reacting species and catalyst are presented in Table 6.

Table 3. Properties of feed and products of FCC [20]

Component	**API Gravity**	**Composition, (wt. %)**	**Flow rate (kg/s)**
Gas-oil feed	21.2	100	67.8
Fuel gas	-	5.4	3.66
C_3 LPG	-	6.3	4.27
C_4 LPG	-	10.7	4.27
Gasoline	60.0	45.9	31.12
Light cycle oil	14.0	17.8	12.07
Bottoms	0.5	8.8	5.97
Coke	-	5.1	3.46

Table 4. Dimensions of some components of FCC unit [20]

Parameter	**Value (m)**
Reactor height	22.9
Reactor diameter	2.9
Cyclone height	14.24
Cyclone diameter	1.5
Disengager height	24.49

Table 5. Feedstock composition [20]

Hydrocarbon	**% Mass**
Paraffins	35.4
Naphthenes	16.1
Aromatics	48.5

Table 6. Physcial properties of reacting species and catalyst [12]

Parameter	**Value**
Vapour density, kg/m^3	9.52
Liquid density, kg/m^3	924.8
Specific heat of gas, kJ/kg K	3.3
Specific heat of liquid, kJ/kg K	2.67
Heat of vapourization, kJ/kg	156
Bulk density of catalyst, kg/m^3	975
Particle size of catalyst, m	75×10^{-6}
Specific heat capacity of catalyst, kJ/kg K	1.12
Mass flowrate of catalyst from the riser to regenerator, kg/hr	1729750

5. Results and Discussion

Table 7 shows the comparison between plant data and model-predictions of the catalytic cracking of gas-oil based on the six-lump kinetic scheme, indicating that the model-predictions compare reasonably well with the plant data.

Table 7. Comparison between model-predictions and plant data of FCC riser-reactor

Parameter	Plant data	Model-prediction
Ga-oil (wt.%)	26.6	26.66
Gasoline (wt.%)	45.9	45.81
LPG 4 (wt.%)	10.7	10.68
LPG 3 (wt.%)	6.3	6.32
Fuel Gases (wt.%)	5.4	5.42
Coke (wt.%)	5.1	5.11
Riser outlet-temperature, K	658	660.94

Figure 2 shows the variations of mass fraction of gas-oil and the various products of the catalytic cracking process with the dimensionless height of the riser-reactor, indicating that the mass fraction of gas-oil decreases as the height of the riser-reactor increases, while the mass fractions of gasoline, LPG, fuel gas, and coke, increase as the riser-height increases. As gas-oil enters the riser-reactor, it is cracked into the various products as it is conveyed up the reactor in contact with the catalyst.

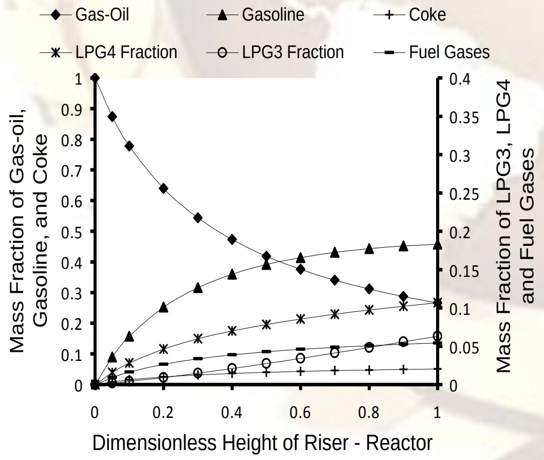

Fig. 2. Variations of mass fraction of gas-oil and products of catalytic cracking with dimensionless height of riser-reactor

The rate of cracking of gas-oil and the contact time of gas-oil and catalyst, increase as the height of the riser-reactor increases. Hence, the mass fraction of gas-oil decreases from an initial value of unity (=1) at the inlet of the riser-reactor to a minimum value at the outlet of the reactor, while the mass fraction of individual product increases from an initial value of zero from the inlet of the riser-reactor to a maximum value at the outlet of the reactor.

The dependence of the yield of the various products of the catalytic cracking process on the fractional conversion of gas-oil is shown in Fig. 3, indicating that the fractional yield of each product increases as the fractional conversion of gas-oil increases.

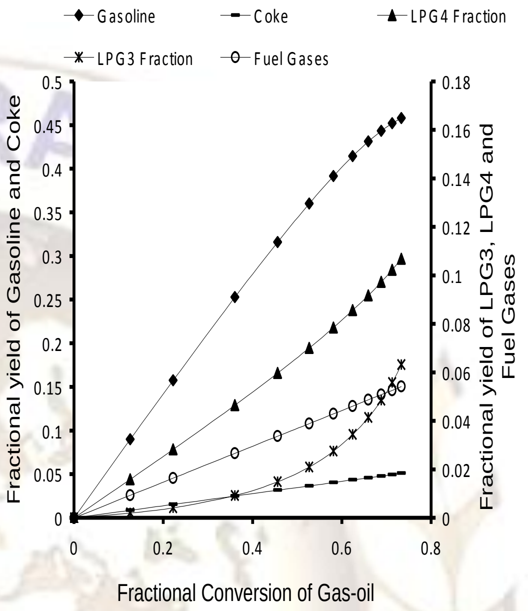

Fig. 3. Dependence of yield of products of catalytic cracking on fractional conversion of gas-oil

This is a result of the cracking of gas-oil to form the various products whose yields increase as the conversion of gas-oil increases.

Figure 4 shows the temperature progression along the riser-reactor, where the temperature inside the reactor decreases from an inlet value of about 800K to about 660K at the exit of the reactor. Since the endothermic cracking reactions take place along the riser-reactor, and the rate of cracking increases with the height of the reactor, the heat absorbed by the cracking reactions also increases with the height of the riser-reactor while the temperature in the riser-reactor decreases as the height of the reactor increases as obtained in Fig. 4.

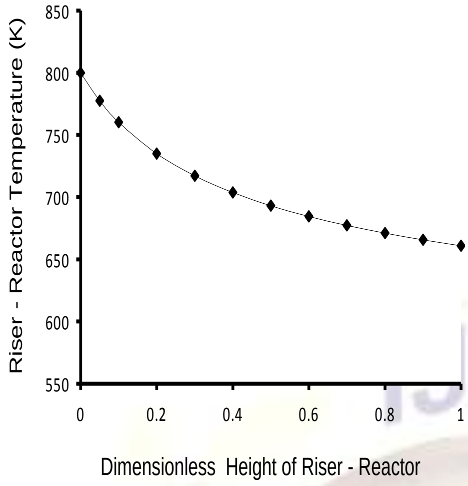

Fig. 4. Steady-state temperature profile along the riser-reactor

However, the temperature at any point along the riser-reactor does not change with time which means that the riser-reactor operates at steady-state.

5.1. Sensitivity Analysis

A simulation model can be used to optimize plant performance by choosing the optimal set of operating conditions such as temperature, pressure, flowrate, etc. In this work, the effects of inlet-temperature of gas-oil, catalyst-to-gas oil ratio, and mass flowrate of gas-oil, on the yield of products and outlet-temperature of the riser-reactor are investigated.

Figure 5 shows the effect of inlet-temperature of gas-oil on the mass fractions of gas-oil and products of the catalytic cracking process, indicating that the mass fractions of gas-oil and products of the catalytic cracking process are practically independent of the inlet-temperature of gas-oil until 900K, beyond which, the mass fractions of the products decrease sharply while the mass fraction of gas-oil increases tremendously. Inspection of Figs. 2, 3, and 5 reveals that the linear section of the profile for gas-oil in Fig. 5 corresponds to the minimum mass fraction of gas-oil, while the linear part of the profiles (Fig. 5) for the various products of the cracking process corresponds to the maximum mass fraction of the respective products. This suggests that one or more of the simulated operating conditions of the riser-reactor (e.g. catalyst-to-gas oil ratio of 6.5, gas-oil mass flowrate of 67.8 kg/s; inlet-temperature of gas-oil of 505K) give(s) maximum conversion of gas-oil with corresponding maximum yield of products.

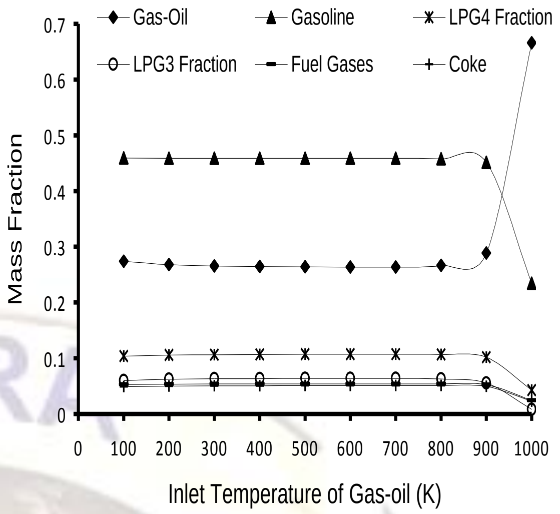

Fig. 5. Variations of mass fraction of gas-oil and products of catalytic cracking with inlet-temperature

When the conversion of gas-oil is maximum, the rate of cracking of gas-oil and the quantity of heat absorbed by the endothermic cracking reactions are also maximum, so that any increase in the inlet-temperature of gas-oil up to 900K does affect the maximum conversion of gas-oil. Beyond gas-oil inlet-temperature of 900K, the catalyst becomes deactivated and the rate of cracking decreases greatly, so that the quantity (and mass fraction) of uncracked gas-oil in the riser-reactor increases while the yield (and mass fraction) of the products decreases accordingly as obtained in Fig. 5. Thus, high inlet-temperature of gas-oil up to 900K and above do not favour the catalytic cracking process as it can cause permanent catalyst deactivation and consequent reduction in the conversion of gas-oil and yield of products.

Figure 6 shows the effect of inlet-temperature of gas-oil on the outlet-temperature of the riser-reactor, indicating that the outlet-temperature of the riser-reactor increases nearly proportionately as the inlet-temperature of gas-oil increases up to 900K; thereafter, the outlet-temperature of the riser-reactor rises sharply as the inlet-temperature of gas-oil increases. The nearly proportionate increase in the riser outlet-temperature as the inlet-temperature of gas-oil increases up to 900K is consistent with Fig. 5. Since the rate of cracking of gas-oil is maximum at the simulated operating conditions as explained in the preceding section for Fig. 5, it means the quantity of heat absorbed by the endothermic cracking reactions is also maximum and more heat cannot be absorbed by the cracking reactions.

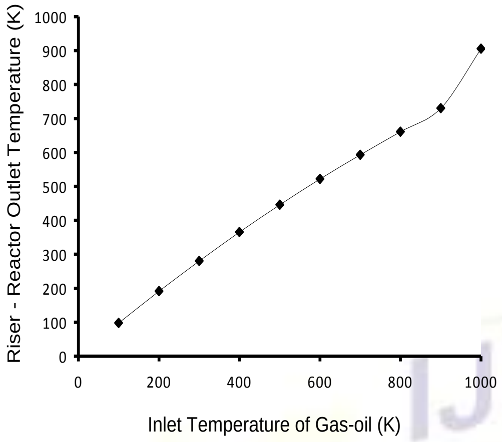

Fig. 6. Variation of riser-reactor outlet-temperature with inlet-temperature of gas-oil

Therefore, any increase in the inlet-temperature of gas-oil results in a corresponding increase in the riser-temperature which is manifested in the outlet-temperature of the riser-reactor as shown in Fig. 6 up to gas-oil inlet-temperature of 900K. Beyond inlet-temperature of gas-oil of 900K, the catalyst becomes deactivated and the rate of cracking of gas-oil decreases so that the quantity of uncracked gas-oil in the riser-reactor increases as explained above. It is the extra heat in the increased quantity of uncracked gas-oil caused by the reduced rate of the cracking reactions that shoots up the riser-temperature and/or outlet-temperature of the riser-reactor for inlet-temperature of gas-oil greater than 900K as obtained in Fig. 6.
Figure 7 shows the effect of catalyst-to-gas oil ratio (CTO) on the mass fractions of gas-oil and the products of the catalytic cracking process. The mass fraction of gas-oil decreases slightly to a minimum value as the CTO increases from 1 to 3, and then remains approximately constant at the minimum value for $\mathrm{CTO} \geq 3$. The slight decrease in the mass fraction of gas-oil for $1 \leq \mathrm{CTO} < 3$ is a result of its conversion to products, with the rate of conversion of gas-oil increasing as CTO increases from 1 to 3.

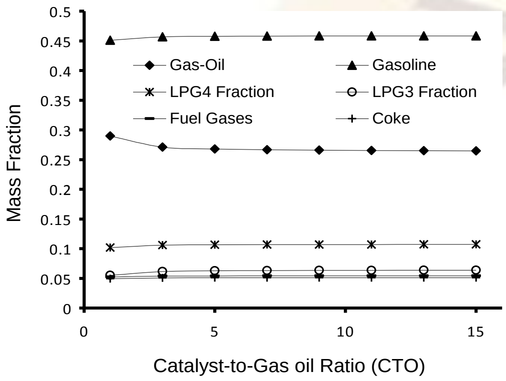

Fig. 7. Variations of mass fraction of gas-oil and products of catalytic cracking with catalyst-to-gas oil ratio

Accordingly, the mass fraction of all the products increases slightly to a maximum value as the CTO increases from 1 to 3; thereafter, the mass fraction of each product remains constant at the maximum value for $\mathrm{CTO} \geq 3$. Increasing the CTO means increasing the mass flowrate of catalyst entering the reactor with respect to the mass flowrate of gas-oil. With more catalyst available in the riser-reactor, the number of active sites of catalyst for the cracking reactions also increases resulting in increased conversion of gas-oil to products, but the catalyst spends less time in the riser-reactor at high CTO than at low CTO. Thus, a minimum value of $\mathrm{CTO} = 3$ is recommended for maximum conversion of gas-oil, and the value of CTO = 6.5 used in the present simulations is consistent with Fig. 7 which also confirms the results in Fig. 5.

Figure 8 shows the effect of catalyst-to-gas oil ratio on the outlet-temperature of the riser-reactor, indicating that the outlet-temperature of the riser-reactor decreases slightly from about 668K to a minimum value of 660K as the CTO increases from 1 to 3; thereafter, the riser-reactor outlet-temperature remains practically constant at the minimum value for $\mathrm{CTO} \geq 3$.

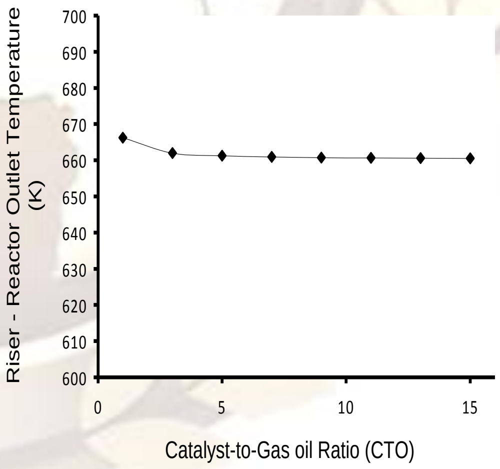

Fig. 8. Variation of riser-reactor outlet-temperature with catalyst-to-gas oil ratio

The slight decrease in riser-reactor outlet-temperature for $1 \leq \mathrm{CTO} < 3$ is due to the heat absorbed by the endothermic cracking reactions of gas-oil and is consistent with Fig. 7 for the same range of CTO. For $\mathrm{CTO} \geq 3$, the rate of cracking of gas-oil is maximum and remains constant at the maximum value. With maximum rate of cracking of gas-oil, the quantity of heat absorbed by the endothermic cracking reactions is also maximum, resulting in a constant outlet temperature of the riser-reactor for $\mathrm{CTO} \geq 3$ as obtained in Fig. 8.

Figure 9 shows the effect of mass flowrate of gas-oil on its mass fraction and mass fraction of products of the catalytic cracking process., indicating that the mass fraction of gasoline increases to a maximum value of about 0.46 corresponding to mass flowrate of gas-oil of about 50 kg/s; thereafter, the mass fraction of gasoline decreases as the mass flowrate of gas-oil increases.

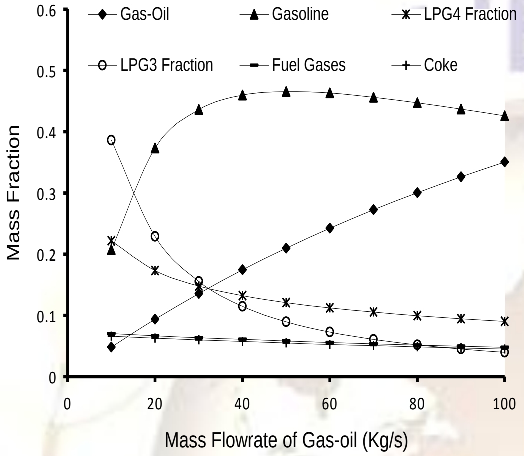

Fig. 9. Variation of mass fraction of gas-oil and products of catalytic cracking with mass flowrate of gas-oil

The mass fraction of gas-oil increases nearly linearly as its mass flowrate increases, while the mass fractions of the other products (except gasoline) decrease as the mass flowrate of gas-oil increases. We note that CTO = 6.5 was used in Figs. 2 – 10; therefore, increasing the mass flowrate of only gas-oil while that of the catalyst remains constant, means decreasing the CTO with the effect that the contact time of gas-oil and catalyst decreases. Thus, as the mass flowrate of gas-oil increases, the contact time of gas-oil and catalyst decreases, and the rate of the endothermic cracking reactions and yield of products also decrease, which is not fully satisfied by only gasoline (see Fig. 9). The initial increase in the mass fraction of gasoline as the mass flowrate of gas-oil increases may partly be attributed to (i) a balance between the reduced contact time of catalyst and gas-oil, and the increased quantity of gas-oil entering the riser-reactor per unit time, so that the rate of cracking of gas-oil increases, and (ii) the effect of zeolite catalyst most often used in FCC which exhibits the unique property of selectively enhancing the yield of gasoline. Beyond mass flowrate of gas-oil of 50 kg/s, the contact time of gas-oil and catalyst becomes too short to sustain efficient cracking of gas-oil, so the mass fraction of gasoline decreases. On the other hand, the continuous increase in the mass fraction of gas-oil (despite its conversion to gasoline and other products) as the mass flowrate of gas-oil increases, indicates that the overall rate of the endothermic catalytic cracking reactions decreases as the mass flowrate of gas-oil increases so that the quantity (and mass fraction) of uncracked gas-oil in the riser-reactor increases as the mass flowrate of gas-oil increases as obtained in Fig. 9. (It is worthy of note from Fig. 9 that although the rate of cracking of gas-oil to gasoline increases to some extent as the mass flowrate of gas-oil increases, the rates of all the other cracking reactions in the six-lump kinetic model (Fig. 1) decrease as the mass flowrate of gas-oil increases; this justifies the decrease in the overall rate of the endothermic cracking reactions as the mass flowrate of gas-oil increases).

Figure 10 shows the effect of mass flowrate of gas-oil on the riser-reactor outlet-temperature, indicating that the riser-reactor outlet-temperature increases as the mass flowrate of gas-oil increases.

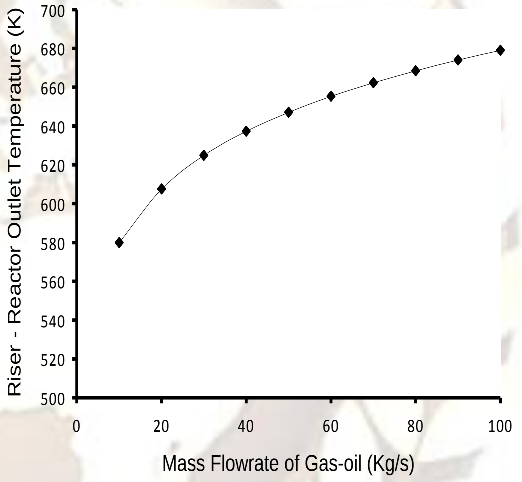

Fig. 10. Variation of riser-reactor outlet-temperature with mass flowrate of gas-oil

It may be necessary to indicate that the total quantity of heat in the riser-reactor is supplied partly by the regenerated catalyst from the regenerator and partly by the gas-oil entering the riser-reactor. Since gas-oil enters the riser-reactor at a constant temperature, both the quantity of heat generated by only gas-oil in the riser-reactor and the total quantity of heat in the reactor increase as the mass flowrate of gas-oil increases. Given that the overall rate of the endothermic cracking reactions taking place in the riser-reactor decreases as the mass flowrate of gas-oil increases, the total quantity of heat absorbed by catalytic cracking reactions also decreases as the mass flowrate of gas-oil increases, such that the riser-temperature and/or outlet-temperature of the riser-reactor increases as the mass flowrate of gas-oil increases as obtained in Fig. 10.

6. Conclusion

A six-lump kinetic scheme which describes the catalytic cracking reactions taking place in an adiabatic plug-flow riser-reactor has been presented. The advantage of the six-lump kinetic model is that it allows independent predictions of C_3's and C_4's. It is shown that catalyst-to-gas oil ratio, inlet-temperature of gas-oil, and mass flowrate of gas-oil, have significant effects on the operation of the riser-reactor, and a minimum catalyst-to-gas oil ratio of 3 is required for maximum conversion of gas-oil. Simulation results presented in the study using catalyst-to-gas oil ratio of 6.5, inlet-temperature of gas-oil of 505K, and mass flowrate of gas-oil of 67.8 kg/s, give yields of 45.81% gasoline, 6.32% C_3's, 10.68% C_4's, 5.42% fuel gas, 5.11% coke, and 26.66% of unconverted gas-oil.

Nomenclature

A_R	cross-sectional area of the riser-reactor, m^2
C_i	molar concentration of lump i, kmol/m^3
Cp_{cat}	specific heat capacity of the catalyst in the riser-reactor, kJ/kg K
C_{po}	specific heat capacity of gas-oil in the riser-reactor, kJ/kg K
CTO	catalyst-to-gas oil ratio
D_{eff}	effective diffusivity of gas-oil through the catalyst, m^2/s
D_p	pre-exponential factor for diffusion used in eq. (16), m^2/s
E_D	activation energy for diffusion used in eq. (16), kJ/kmol
F_o	mass flowrate of gas-oil, kg/s
F_{cat}	mass flowrate of catalyst, kg/s
h_i	modified Thiele modulus used in eq. (12).
h_o	modified Thiele modulus for gas-oil used in eq. (15).
k_d	catalysts decay coefficient used in eq. (8), s^{-1}
k_{do}	catalyst decay pre-exponential kinetic factor used in eq. (8), s^{-1}
k_{ij}	intrinsic rate constants of species i, m^3/kg kmol s or m^6/kg kmol s
k_{io}	pre-exponential (or Arrhenius) factor used in eq. (36), m^3/kg kmol s or m^6/kg kmol s
L_R	height of riser-reactor, m
L_z	characteristic dimension of Zeolite crystallite used in eq. (14), m
M_i	molecular weight of lump i used in eqs. (37)-(48), kg/kmol
r_i	rate of cracking species i, s^{-1}
R	universal gas constant, kJ/kmol K
t	time, s
T	absolute temperature, K
T_{ref}	reference temperature, K
T_R	temperature of riser-reactor, K
V_{ij}	stoichiometric ratio of lump i to lump j defined in eqs. (37)-(48).
y_i	mass fraction of component i
Z	dimensionless height of riser-reactor.

Greek Letters

α_{ext}	catalyst-specific external surface area used in eq. (14), m^{-1}
ε_R	average void fraction in the riser-reactor
ρ_o	mass density of gas-oil, kg/m^3
ρ_{cat}	mass density of catalyst, kg/m^3
ρ_i	mass density of lump i, kg/m^3
ρ_T	total mass density of all lumps defined after eq. (6), kg/m^3
ΔH_{ij}	heat of reaction for cracking lump i to j, kJ/kmol
ϕ	catalyst deactivation function.
θ_R	dimensionless temperature of riser-reactor
ϑ_o	volumetric flowrate of gas-oil used in eq. (27), m^3/s
η_{ss}	effectiveness factor

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